

UDC 666.295:546.7.73

EFFECT OF DEXTRIN ON PROPERTIES OF GLAZES AND CERAMIC PAINTS AND ON THE REDUCTION OF COBALT OXIDE

N. S. Rusovich-Yugai¹

Translated from *Steklo i Keramika*, No. 3, pp. 20–22, March, 2006.

It is established that dextrin contained in cobalt-bearing paints influences the quality of decorative ceramics. The content of dextrin is responsible for the probability of such defects as paint crumbling and cobalt metallization. As the content of dextrin in a paint grows and its adhesive capacity increases, the glaze layer thickness at the sites of paint application decreases, as well as the viscosity, the wetting angle, and the porosity of glaze. It is recommended to introduce 13% dextrin into cobalt-bearing paints.

Ceramic paints used to decorate ceramic products contain different additives such as dextrin, glycerin, glucose, sugar, etc. These additives regulate the properties of the paint, such as elasticity or binding and adhesive capacity. Improper application of such additives in the production of paints may increase the percentage of products rejected after firing as a consequence of defects that appear in the paint after its fixing.

The experience of artists painting porcelain and faience shows that the above specified additives in ceramic paints are necessary prerequisites to hand painting. Frequent defects are “cobalt metallization” and exfoliation of paint (Fig. 1), which can be observed at the sites of thick application of cobalt paint and a decreased thickness of the glaze layer.

To identify the reasons for the glaze layer thickness decreasing at the sites where a thick cobalt paint layer is applied and for paint exfoliation, we isolated the adhesive additive, i.e. dextrin from the paint mixture, in order to investigate its properties. Dextrins (products of starch processing) differ according to their adhesive capacity, the degree of solubility, and the type of initial material. Depending on their

properties, dextrins may cause different defects not only in the paint layer of porcelain articles but also in the glaze coating. We have investigated dextrins whose characteristics are listed in Table 1.

A portion of 2 g of each dextrin under study was dissolved in an equal quantity of water: 10 ml. The dextrin solutions were applied using a brush on fired ceramic tiles that were covered with a glaze suspension and fired at a temperature of 1350°C.

It was found that samples with dextrin samples 2, 4, and 5 had discontinuities in the glaze layer and a lower extent of dryness than samples 1 and 6; sample 3 exhibited an insignificant decrease in the glaze layer thickness.

The petrographic analysis of dextrin samples 3 and 6 revealed a variation in the glaze layer thickness on the sites subjected to the effect of dextrin. We have arbitrarily categorized three areas (Table 2): I) glaze without dextrin; II) the boundary glaze layer; III) glaze with dextrin.

The different effect of particular varieties of dextrin should be attributed to their adhesive capacity; as this capacity increases, the paint more tightly seals the pores of the ceramic substrate and prevents it from absorbing the glaze suspension. Consequently, dextrin already at the stage of glazing

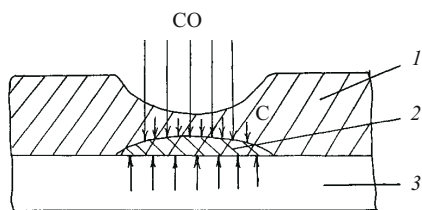


Fig. 1. The scheme of the glaze profile at the sites of applying cobalt paint and without paint: 1) glaze, 2) paint, 3) porcelain.

TABLE 1

Dextrin	Characteristic	Degree of solubility, %
1	Potato, acid	33
2	The same	63
3	"	98
4	Potato, alum	70
5	Corn, acid	60
6	The same	98

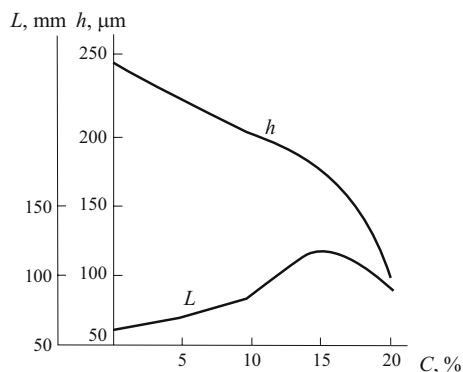


Fig. 2. The effect of dextrin content C on glaze layer thickness h and the spreading length of the glaze melt L .

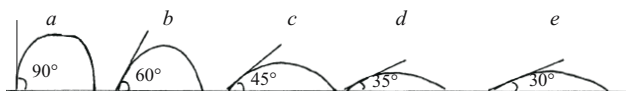


Fig. 3. Scheme of contact wetting angle for glaze drops: *a*) glaze without dextrin; *b, c, d, e*) glaze with 5, 10, 15, and 20 % dextrin, respectively.

contributes to decreasing the glaze coating thickness, whereas under firing it decomposes, releasing carbon and freeing the ceramic substrate pores from the effect of dextrin. The decrease in the glaze layer thickness and the dryness on the sites subjected to the effect of dextrin after firing are due to the fact that free pores in ceramics absorb the glaze melt.

To corroborate the effect of dextrin on the glaze layer, we prepared solutions containing 10, 15, and 20% dextrin. Ceramic samples were coated with these solutions, then glazed, and fired. After firing the maximum decrease in the glaze layer thickness was registered on the sites covered with dextrin of the maximum concentration.

Thus, variations of the glaze layer thickness depend on the concentration of dextrin in the glaze composition. On introducing 10–15% dextrin in the cobalt paint, the thickness of the glaze layer over the paint is up to 200 μm .

The effect of dextrin concentration on the glaze melt viscosity was studied according to the standard procedure [1]. Four spheroid samples weighing 1 g each were made from glaze mixtures; the content of dextrin in the samples was 0, 10, 15, and 20%. The samples were fired at 1350°C. After firing, the glaze melts had different lengths of spreading. An increased content of dextrin in a glaze decreased the melt

viscosity, which increased the glaze fluidity. The maximum viscosity decrease was achieved by introducing 15% dextrin, and the spreading length of the glaze melt was 124 mm. On further increasing the content of dextrin to 20% the glaze spreading site decreased to 98 mm, i.e., the fluidity of the glaze dropped and, accordingly, its viscosity grew. The variation in glaze viscosity depending on dextrin content is shown in Fig. 2 (the length of spreading of the initial glaze sample without dextrin is taken as 100%).

The variation of the contact glaze wetting angle was determined on five samples molded as cylinders of height 10 mm and diameter 30 mm from glaze mixtures containing 0, 5, 10, 15, and 20% dextrin. The samples were placed on ceramic tiles and fired at a temperature of 1350°C. The glaze in firing spreads in drops over the surface of the ceramic tile (Fig. 3). The following regularity was observed: as the content of dextrin grows, the contact wetting angle decreases and, accordingly the surface tension and viscosity of glaze decrease as well.

When fired in a reducing medium, where the furnace gas may contain free carbon and where at 327°C and the furnace pressure 0.1 MPa the content of carbon monoxide sharply grows, the probability of “cobalt metallization” increases. It is further stimulated by the fact that dextrin ($\text{C}_6\text{H}_{10}\text{O}_5$)_x contained in the cobalt paint decomposes in a reducing medium and releases free carbon, which acts as another factor in reducing cobalt oxide. The thermogram of dextrin has peaks at temperatures of 110, 246, and 438°C corresponding to the water removal and decomposition of dextrin. It is known that carbon creates a reducing gaseous medium close to equilibrium. This is corroborated by experimental data described below.

An artist hand-painting an article applies brushes converging them in a single point (brushed are superimposed on each other). The point of convergence of several brushes contains a larger amount of dextrin, therefore, a small crater is formed here testifying the the penetration of the low-viscosity glaze melt into the porous ceramics. Therefore, the glaze layer thickness decreases on sites with an increased content of dextrin.

In decorating porcelain articles by underglaze hand painting using a blue paint based on spinel $\text{Mg}_{0.68}\text{Co}_{0.32}\text{Al}_2\text{O}_4$ and cobalt oxide, the maximum content of cobalt oxide in the paint was found equal to 40%. Raising the content of cobalt oxide in the paint above 40% leads to cobalt metallization (Table 3).

The crumbling of cobalt paint off the ceramic surface is also influenced by the content of dextrin in the paint. It was

TABLE 2

Dextrin	Glaze layer thickness, μm , in areas			Porosity of glaze, %, in areas			Mean pore diameter, μm , in areas		
	I	II	III	I	II	III	I	II	III
3	300	250	80	5.1	5.0	4.9	32	30	27
6	300	250	50	5.1	5.0	1.0	32	30	14

TABLE 3

Sample	Spinel synthesis temperature, °C	Weight content, %		Cobalt metallization defect
		of pignut $\text{Mg}_{0.68}\text{Co}_{0.32}\text{Al}_2\text{O}_4$	of cobalt oxide	
1	700	100	—	No
2	800	100	—	"
3	900	100	—	"
4	700	60	40	"
5	800	60	40	"
6	900	60	40	"
7	700	50	50	Exists
8	800	50	50	"
9	900	50	50	"
10	800	40	60	"
11	900	40	60	"

experimentally established that the optimum content of dextrin should be 13 – 16% (Table 4). In this case the crumbling of cobalt paint in the course of glazing stops. It has also been established that introducing 15% dextrin in a paint mixture decreases the glaze layer thickness from 250 to 180 μm . Increasing the content of dextrin above 15% may sharply decrease the glaze layer thickness up to its complete disappearance and thus degrade the protective function of glaze, which may cause the metallization of cobalt.

It is known that the quality of a glaze coating depends on the interaction between glaze and ceramics, resulting in gaseous bubbles from ceramics penetrating into the glaze coating. It also depends on the processes taking place in glaze itself after the appearance of gas bubbles as a consequence of glass formation, for instance, decomposition of carbonates, desorption of the dissolved and absorbed gaseous phase, etc.

Thus, cobalt oxide in a cobalt-bearing paint at the ceramic – glaze interface is reduced to its metallic state due to the effect of gases penetrating from the furnace space, from

TABLE 4

Sample	Content of dextrin in paint, %	Surface area of exfoliated paint	
		mm^2	%
1	—	31.4	1.93
2	3	23.0	1.42
3	5	15.7	0.97
4	8	7.9	0.49
5	10	5.1	0.31
6	13	—	—
7	16	—	—
8	20	11.0	0.68

the ceramics, and from the glaze itself through its pores. The effect of gases on the reduction of cobalt oxide depends on the quantity and size of glaze pores. Since the thickness of the glaze layer decreases at the sites subjected to the effect of dextrin and, accordingly, the pores becomes larger, cobalt oxide contained in the ceramic paint becomes unprotected from the effect of the reducing medium. Furthermore, dextrin decomposes under firing releasing carbon, which contributes to the additional formation of a highly reducing medium in the paint layer. All this creates conditions for reducing cobalt oxide to its metallic state.

By controlling the content of dextrin in a paint and taking into account the adhesive capacity of dextrin, one can diminish the presence of such defects as crumbling of paint and metallization of cobalt in the production of decorated ceramics. It is recommended to introduce 13% dextrin into a cobalt-bearing paint.

REFERENCES

1. I. Ya. Yurchak, A. I. Avgustinik, A. S. Zaporozhets, et al., *Methods of Study and Control in Porcelain and Faience Production* [in Russian], Legkaya Industriya, Moscow (1971).